Full Length Research

Dennettia tripetala extract as green corrosion inhibitor of mild steel in Hydrochloric acid.

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The inhibiting action of *Dennettia tripetala* extract on corrosion of mild steel in 1M HCl solution was examined using gravimetric technique. The results showed that *Dennettia tripetala* extracts (leave, stem and root) reduced the rate of corrosion in 1M HCl and inhibition efficiency increased with increase in concentration of the extract. Adsorption characteristics of the extract are approximated by Langmuir isotherm. The inhibition mechanism estimated from temperature dependence of inhibition efficiency as well as activation parameters show that the extracts inhibits corrosion via physical adsorption of the extract on the surface of the mild steel.

Keywords: Mild steel, Corrosion Inhibition, *Dennettia tripetala*, Adsorption mechanism

INTRODUCTION

Metallic materials are extensively used in industries, where they are exposed to aggressive environments. Excessive corrosion is known to occur on metals deployed in service in these aggressive environments. To protect such metals from corrosion, corrosion inhibitors such as inorganic substances like phosphates, chromates dichromates, silicates, borates, tungstates, molybedates and arsenates were introduced to reduce the corrosion rate. These inorganic inhibitors have been found effective as inhibitors of metal corrosion Oguzie (2008). Regrettably the inhibitors face severe criticism because of their toxicity. Among the alternative corrosion inhibitors, organic substances containing polar functions with nitrogen, oxygen and sulphur, in the conjugated system have been reported to exhibit good inhibiting properties. Quvaishi and Sharma (2005).Following these findings, natural products of plant origin containing these polar functions have been recently employed in the inhibition of metallic corrosion. Buchweishaija (2009) Besides being environmentally friendly and ecologically acceptable these natural products are inexpensive, readily available and renewable sources of materials.

In this study investigation is carried on the inhibitory effect of *Dennettia tripetala* leave, root and stem extract on corrosion mild steel in acidic media using gravimetric technique.

Dennettia tripetala is a well-known forest spicy fruit, commonly known in English as pepper fruit. It is widely found and used for numerous purposes in southern Nigeria, within West Africa it is a common ethno medicinal plant and can be used to treat cough and enhance appetite. Aside medicinal value it also possess insecticidal properties. Ejechi et al (1999), Okogun (1969) and Okwu (2004) stated that *D. Tripetela* Contains essential oils and phenolic acid, ethanol, ethyl acetate, flavanoid, tannin and glycoside. Further isolations on *D. Tripetela* showed that it contain vanillin, 2,6-dimethoxy chromone argertine and uvariopsin Janvier (2002). Elemental analysis showed that it contains mainly Ca, Fe and other elements like Mg, Zn, Mn and Co. Generally the fruits contain minerals, vitamins, flavouring oils, crude proteins, fibre ach, carbon and sulphur. Udoessien (1984) Equiped with this information about *Dennettia tripetala*, we reasoned it will be interesting employing the extract of this plant in corrosion studies.

To the best of our knowledge nothing has been reported on the use of *Dennettia tripetala* root, leave and stem extracts respectively on corrosion inhibition. The present study investigates the inhibitory effect of *Dennettia tripetala*, leave, stem and root extracts on corrosion of mild steel in acidic medium, using gravimetric technique.

Table 1: *Dennettia tripetala* leave extract

System (mg/l)	Weight loss (g)	Corrosion rate (mdd)	Surface coverage(θ)	Inhibition efficiency (%)
Blank	0.0140	3.2385		
200	0.0110	2.5445	0.2143	21.43
400	0.0090	2.0819	0.3571	35.71
600	0.0085	1.9662	0.3929	39.29
800	0.0065	1.5036	0.5357	53.57
1000	0.0050	1.5660	0.6429	64.29

Table 2: Dennettia tripetila Root extract

System (mg/l)	Weight loss (g)	Corrosion rate (mdd)	Surface coverage(θ)	Inhibition efficiency (%)
Blank	0.014	3.2385		
200	0.0085	1.9662	0.3929	39.29
400	0.0070	1.6193	0.5000	50.00
600	0.0065	1.5036	0.5357	53.57
8000	0.0055	1.2723	0.6071	60.71
1000	0.0045	1.0409	0.6786	67.86

Table 3: Dennettia tripetila stem extract

System (mg/l)	Weight loss (g)	Corrosion rate (mdd)	Surface coverage (θ)	Inhibition efficiency (%)
Blank	0.0140	3.2385		
200	0.0105	2.4289	0.2500	25.00
400	0.0085	1.9662	0.3929	39.29
600	0.0075	1.7349	0.4643	46.43
8000	0.0060	1.3879	0.5714	57.14
1000	0.0045	1.0409	0.6786	67.86

MATERIALS AND METHODS

Mild steel sheets used for the study were of weight composition, C. 0.05% Mn; 0.60%, P:0.36, Si: 0.03% and the rest Fe. The sheets were mechanically press-cut into test panels of dimension 3 x 3cm and a hole drilled at the centre of the coupons with radius 2.5mm. Its thickness is 1mm. Each coupon was degreased in absolute ethanol, dried in acetone, weighed and stored in moisture free desiccators prior to use. Oguzie and Ebenso (2006).

All chemicals and reagents used were analar grade. The blank corrodent was 1M HCl solution. Stock solutions of the plant extract were prepared by refluxing weighed amount of the dried and grounded samples of *Dennettia tripetala* leaves, stem and root separately for 3 hours in 1MHCl solution. The resulting solution were cooled then filtered and stored. From the respective stock solutions inhibitor test solutions were prepared in concentrations range of 200-1000 (mg/l) Oguzie (2008).

Gravimetric experiments

The weight loss experiments were conducted under total immersion conditions in 250ml of test solution maintained at room temperature and 323k for 3 hours. The mild steel coupons were retrieved after the 3hrs scrubbed with bristle brush under running water until clean. The cleaned test coupons were dried in acetone and reweighed. The weight loss was taken as the difference between the weight of the test coupons before and after immersion, according to equation below

$$\Delta W_t = W_{t_i} - W_{t_f} \quad \text{...............} \quad (1)$$

Where ΔW_t is weight loss, W_{t_i} is initial weight before immersion and W_{t_f} is weight of the coupon after immersion.

RESULTS AND DISCUSSION

Weight loss and corrosion rate (ρ)

The corrosion rate of the mild steel in the absence and the presence of *Dennettia tripetala* root, leave and stem extracts were assessed from the weight loss measurements. The weight loss data for inhibited and uninhibited samples were shown in tables 1, 2 and 3. Table 1 shows the inhibited data sample in various concentrations of the D. Tripetala leaves extract with the uninhibited indicated as blank. Table 2 shows the sample data in various concentrations of root extract and table 3 has the sample data in stem extract.

Table 4: At 50^0C

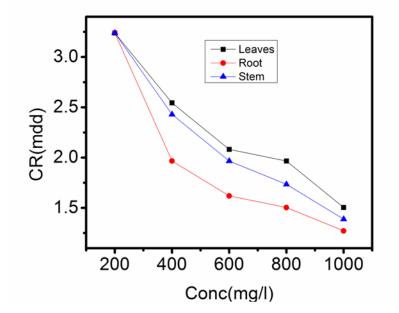| System	Weight Dw (g)	CR (Mdd)	θ	I(%)
Blank	0.032	7.4023		
Stem	0.0250	5.7830	0.2108	21.88
Root	0.033	5.8987	0.2031	20.31
Leave	0.0315	7.2866	0.0150	1.56

Figure 1: Corrosion rate of mild steel with concentrations of *D. Tripetela* extract.

From the data shown the tables 1, 2 and 3, the weight loss values in the inhibited system are smaller than that in uninhibited system. That implies the extracts retard corrosion of mild steel in acidic media by reducing the corrosion rate. The corrosion rate (ρ) was calculated from equation 2 below:

$$\rho = \frac{\Delta W}{AT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . 2$$

Where Δw is equal to weight loss, A is area of the coupon and T is equal to period of immersion. From the data represented in Figure (1) the corrosion rate decreases as the concentrations of the *D. Tripetela* extract increases, showing that the degree of inhibition depends on the concentration of the extract present in the system.

Inhibition efficiency

The inhibition efficiency was calculated from the equation

$$IE(\%) = (1 - \frac{\rho_{in}}{\rho_{bl}}) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3$$

Where IE is inhibition efficiency, ρ_{in} and ρ_{bl} corresponds to corrosion rates in inhibited and uninhibited systems respectively.

In Figure 2 the plot of inhibition efficiency against concentrations of the *D. Tripetela* leaves, root and stem extract are shown. From the graph the inhibition efficiency was found to increase as the concentration of the extracts increases. From the data it is observed that inhibition was more efficient in root and stem extract than that of leave which has inhibition efficiency of 64.29% at 1000(mg/l) with both stem and root extract having inhibition efficiencies of 67.36 respectively. The observed inhibition can be attributed to the adsorption of the extract on the metal surface. As the inhibitor gets adsorbed to the metal surface corrosion rates then depends on the number of corroding sites remaining. Assuming corrosion occurs only on the free sites such that the covered sites has zero corrosion rate, the degree of surface coverage (θ) is calculated with equation 4 below

$$\theta = (1 - \frac{P_{in}}{P_{blank}}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. \ldots\ldots\ldots 4$$

Absorption of the extract on the metal surface can be attributed to alkaloids contained in *D. Tripetela* Isolations carried on *D. Tripetela* by Jauier et al. (2002) Rossana et al (2004) shown that *D. Tripetela* contains alkaloids like Uvariopsine, stephenanthrine, argetinine, vanilline and chromone. These compounds except chromone are
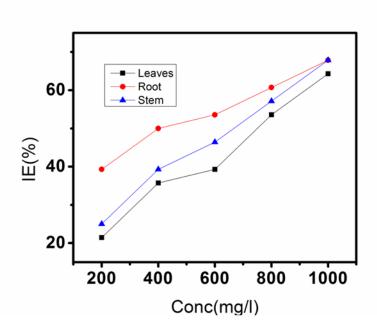
Figure2. Variation of inhibition efficiency against concentration of *D. tripetela* extract(leave, root and stem)

amines and can therefore form complexes with the metal (Fe) by the ability of the amines to bond with iron with the lone pairs from nitrogen to which they donate to the orbitals of the metal. Chromone being a ketone gets absorbed to the metal surface by forming Fe II chromone complex. According to Riggs (1973), Buchweishaika (1997); Raja and Sethuraman (2008) as reviewed in Buchweishaija (2009) organic molecules containing heteroatoms such as nitrogen, sulphur, phosphorous and oxygen show significant inhibition efficiency. This explains the inhibitory ability of *D. Tripetela* extracts on corrosion of mild steel in acidic media. But since *D. Tripetela* contain more than one alkaloid of which all of them have inhibiting abilities, it is difficult to assign the observed inhibiting effect to a particular constituent. The net adsorption of the organic matter on the corroding steel surface creates a barrier that isolates the metal from the corrodent. Oguzie (2008)

Figure 3 represent relationship between the concentration of *D. Tripetela* extract Conc and C/θ for mild steel in *D. Tripetela* leave, stem and leave extracts respectively. It is observed from the Figure that every relation give a straight line with almost unit slope. These results indicate that the adsorption of *D. Tripetela* leave, stem and root extracts molecules on the tested metal in different concentration follow Langmuir adsorption isotherm El-Etre and El-Tantawy (2006) Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and adsorbent Eddy and Ebenso (2008). Adsorption of Langmuir relates the concentration(C) of

the adsorbate in the bulk of the electrolyte to the degree of surface coverage (θ) according to equation 5.

$$\frac{C}{\theta} = \frac{1}{K} + C \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots .5$$

Where K is the equilibrium constant of adsorption.

When values of C/θ is plotted against Conc a straight line graph is obtained as in Figure 3. On applying langmuir adsorption isotherm to the adsorption of *D. Tripetela* on mild steel the formation of multimolecular layer of adsorption is confirmed, where there is no interaction between the adsorbate and the adsorbent. Eddy (2008)

As reported by El-Etre (2006) Langmuir isotherm postulates that the interacting force between the adsorbed molecules and the free energy of adsorption (ΔG_{ad}) does not depend on the surface coverage (θ). The standard free energy of adsorption were calculated using equation 6

$$\ln K = \ln \frac{1}{55.5} - \frac{\Delta G_{ad}}{RT} \dots \dots \dots \dots \dots \dots \dots \dots \dots . \dots \dots \dots \dots 6$$

Where K is adsorption constant, R is gas constant and T stands for temperature of the system. The value 1/55.5 represents molarity of water, where one molecule of water is replaced by one molecule of inhibitor. The values of ΔG^0_{ad} for the studied systems are listed in the table 5

Observations on the Figures in the table reveals that the values of ΔG^o_{ad} at 323K of *D. Tripetela* extracts (leave, stem and root) studied are negative, suggesting spontaneous adsorption. El-Etre and El-Tantawy (2006). On the contrary ΔG^0_{ad} at 298K in all the samples is positive which suggests that adsorption is not spontaneous
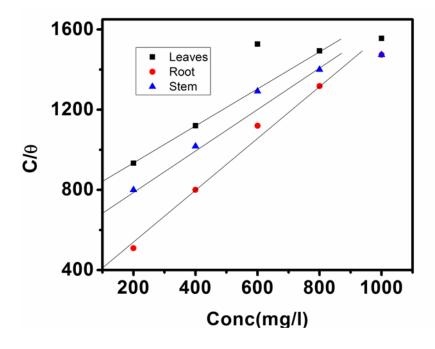
Figure 3. Adsorption isotherms for leave, stem and root extracts of *D. Tripetela*

Table 5: The values of ΔG^0_{ad} for the studied systems

	Stem		Leave		Root	
DG$^0_{ad}$ (KJmol^{-1}K^{-1})	298K	323K	298K	323K	298K	323K
	5.90	-10.79	6.26	-10.77	5.53	-10.78

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Adsorption and Temperature Relations

It was observed that the inhibitor, *D. Tripetela* (root, leave and stem) extract adsorbed to the mild steel at both temperatures studied (298 K and 323K) studied. From the results obtained in this study increase in temperature from 298k to 323K increased the corrosion rate of mild steel both in the absence and presence of the inhibitor. This is because increase in temperature accelerates corrosive process, giving rise to higher dissolution rates of the metal.

Figure 4 Shows a plot of inhibition efficiency of *D. Tripetela* leave stem and root extract against temperature from the Figure. It is observed that inhibition efficiency decreases as temperature increases indicating that the inhibitor was physically adsorbed to metal surface Ferrend (2004). As stated by Hackerman (1954) and Popova et al., (2003) reviewed in Oguzie and Ebenso (2006) inhibitor molecules are either physically or chemically adsorbed on a corroding metal surface, where the physiadsorbed molecules essentially retard

metal dissolution by inhibiting the cathodic reaction while chemisorbed molecules inhibit the anodic reaction by

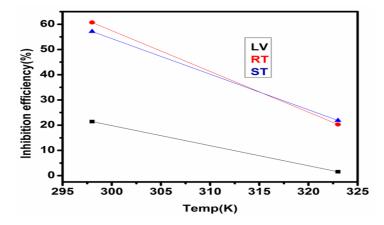reducing the inherent reactivity of the metal at the adsorption site.

Figure 4: Variation of inhibition efficiency against temperature

Thermodynamic and adsorption consideration

Values of activation energy for corrosion of mild steel in and absence of *D. Tripetela* (leave, stem and root) extract have been calculated using equation 7.

$$\rho = A \exp (- Ea/RT) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 7$$

Taking logarithm of both side of equation 7 equation 8 is obtained.

$$\text{Log } \rho = \log A - \frac{E_a}{2.303RT}$$

Where ρ is corrosion rate of the coupon. A, represents Arrhenius constant or pre exponential factors, E_a stands for activation energy of the reaction, R is gas constant and T, temperature. Considering temperature change from 298K (T_i) and 323K (T_2) the values of corrosion rates at these temperatures are ρ_1 and ρ_2 respectively. Inserting these Figures (ρ_1 & ρ_2) into equation 8 we have equation 9

$$\text{Log } \frac{\rho_2}{\rho_1} = \frac{E_a}{2..303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \dots\dots\dots\dots\dots\dots\dots..\dots\dots.. 9$$

The value of the activation energy of the blank system studied is 26.47KJmol^{-1} whereas that of inhibited system of the leave extract is 50.53KJmol^{-1}, the stem extract has activation energy of 45.69KJmoli^{-1} and Root extract with activation energy of 49.11KJmol^{-1}. The activation energy of the inhibited system being greater than that of the blank indicates physiadsorption while the reverse signifies chemisorbtion. The extracts of leave, stem and root of Dennettia tripetela proved to be physically adsorbed to the mild steel surface, having activation energies greater that of the blank, and being less than 80Kjmol^{-1} Ebenso (2003a, b 2004) Sheatty et al., (2006), Eddy and Ebenso (2008).

CONCLUSION

Extracts from leaves, stem, and root of Dennetia tripetala separately subdued mild steel corrosion in 1M HCl at the temperatures studied. Inhibition efficiency increased with an increase in extract concentration. Analyses of experimental result suggest that the extract inhibits corrosion by being physically adsorbed on the metal, surface.

REFERENCES

Buchweishaija J (1997) inhibiting properties and adsorption of an Amine Based fatty acid corrosion inhibitor on carbon steel in aqueous carbon boride solution, Dr. Ing. Avhamding NTNU.

Buchweishaija J (2009) Phytochemicals as green corr. Inhibitors in various corrosive media, reven Anz. J. Sci Val. 35.

Eben EE (2004) Effect at methyl red and halide ions on the corrosion inhibition of aluminum in H_2SO_4. Part 2, Bull Electrochem. 20: 551-559.

Ebenso EE (2003a) Synerepestic effect of halide ions on the corrosion inhibition of aluminium in H_2SO_4 using 2-acetylphonothia-zine. Mater chem. And Phy. 79: 58-70.

Ebenso EE (2003b). Effect of halide ions on the corrosion. Inhibition of mild. Steel in H_2SO_4 using methyl red part 1, Bull Electrochem. 19: 209-216.

Ebenso EE, Okofor PC, Ekpe UJ, Oguzie EE, Umo NS and Eto AR (2006). Trans SAEST 41 p. 82.

Eddy NO. and Ebensor EE (2008) Adsorption and inhibitive properties of ethanol extracts of Masa sapientum peels as a green corrosion inhibitor for mild steel in H_2SO_4 2: 046-054.

Ejechi BO, Nwafor OE, Okoko FJ (1999). Growth inhibition of tomato-rot fungi by

phenolic acids and essential oil extracts of pepperfruit (Dennetia tripetala) Food Res. Intl. 32:395-399.

El-Etre AY (2006) Khillah extract as inhibitor for acid corrosion of SX316 steel Appl. Surface Sci. 252: 8521-8525.

El-Etre AY and El-Tantawy X (2006). Inhibition of medilic corrosion using ficus extract, portugaliae Electrochemica Acta 24: 347-356.

Ferrand, K, Abdelouas A, Grambow B and Crovisier J (2003) The Role

of Water Diffusion in the Corrosion of the French Nuclear Waste Glass SON 68 under Solution Saturation Conditions. Materials Research Society Proceedings vol 87- 193

Ferreira ES, GiaComelli C, Gicomelli FC and Spinelli A (2004) Mater chem.. Phys. 83: 129.

Hackerman N (1964) Effect of adsorption on metal dissolution in aqureous acid solution. Transaction from meeting of electrochemistry section of the New York Academy of science, October 5, P 7-11.

Janview Lopez Martin,Edet M, Herminio B, Sanz Maria Jesus and Maria A

(2002): Chromone and phenanthreneAlkaloids from Chem. and Pharmaceut.Bulletin, 20(12): 1613 5.

Nayak HUS (2006) Inhibition of mild steel corrosion in acid media by N-(2-Thiophenyl-N- phenylthiourea) J. Chil Chem. Sci 51-849-53.

Oguzie EE and Ebenso EE (2006) Studies on the corrosion inhibiting effect of Congo red dye-halide mixtures. Pigment & R.C. Sin Technology 35/1: 30-35.

Oguzie EE (2008) Corrosion inhibitive effect and adsorption behavior of hibiscus sabenffa extract on mildsteel in acidic media. Portugaliae electrochemical ACTA Pp 303-314.

Okogun FI and Ekong DEU (1969): The fragrant principle of fruit of Dennettia

Tripetala Baker: A new naturally occurring Nitro Compound. Chem. and Indust. Lond., 1972 4.

Okwu DE and Morah FN (2004).Mineral and Nutritive Value of D. tripetala.

Fruits 59: 437- 442.

Popova A, Sokelova E, Raicheva S, Christar M (2003) Ac and Dc study of the temperature effect on mild steel corrosion in acid media in the presence of bezimidazole derivatives, Corr. Sci. 45: 33-58.

Riggs OL (1973) Theoretical aspects of corrosion inhibitors and inhibition in corrosion inhibitors by C.C. Nathan (ed), NACE.

Raja, P.N. and Sethuraman, M.G. (2008) National Products as corrosion inhibitors for metals in corrosive media-A review, Material let 62: 113-116.

Sharsma, H.K., Quraishi M,A, (2005). Thiazole as corrosion inhibitor for mild steel in formic and ascorbic media. Apply. Electrochem. 35.

Sheatty D.S, Sheatty P Nayak HVS (2006) Inhibition of mild steel corrosion in acid media by N-(2-thiophenyl) –N-phenyl thiourea. J. Chil. Chem. Soc. 51:849-853

Udoessien EI, Ifon ET (1984): Chemical studies on the unripe and ripe fruits of Dennettia tripetala pepper fruit. Food Chemistry 13(4): 257-263